

**ELECTROCATALYSTS FOR OXYGEN ELECTRODES IN FUEL CELLS
AND WATER ELECTROLYZERS FOR SPACE APPLICATIONS**

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In most instances separate electrocatalysts are needed to promote the reduction of O_2 in the fuel cell mode at to generate O_2 in the energy storage - water electrolysis mode in aqueous electrochemical systems operating at low and moderate temperature ($T \leq 200^\circ C$). This situation arises because, even with relatively high performance catalysts, the O_2 reduction and generation reactions are still quite irreversible with much overpotential. The potentials of the O_2 electrode in the cathodic and anodic modes are separated by typically 0.6 V and the states of the catalyst surface are very different. Interesting exceptions are the lead and bismuth ruthenate pyrochlores in alkaline electrolytes. These catalysts on high area carbon supports have high catalytic activity for both O_2 reduction and generation (1,2). Furthermore, rotating ring-disk electrode measurements provide evidence that the O_2 reduction proceeds by a parallel four-electron pathway. The ruthenates can also be used as self-supported catalysts to avoid the problems associated with carbon oxidation, but the electrode performance so far achieved in the research at CWRU is considerably less. The possibility exists, however, of supporting these catalysts on a stable electronically-conducting high area oxide support such as a perovskite.

At the potentials involved in the anodic mode the ruthenate pyrochlores have substantial equilibrium solubility in concentrated alkaline electrolyte. This results in the loss of catalyst into the bulk solution and a decline in catalytic activity. Furthermore, the hydrogen generation counter electrode may become contaminated with reduction products from the pyrochlores (lead, ruthenium).

A possible approach to this problem is to immobilize the pyrochlore catalyst within an ionic-conducting solid polymer, which would replace the fluid electrolyte within the porous gas diffusion O_2 electrode. For bulk alkaline electrolyte, an anion-exchange polymer is needed with a transference number close to unity for the OH^- ion. Such a membrane may not block completely the transport of the lead and ruthenium, which are expected to be in complex anionic forms. Preliminary short-term measurements with lead ruthenates using a commercially available partially-fluorinated anion-exchange membrane as an overlayer on the porous gas-fed electrode indicate lower anodic polarization and virtually unchanged cathodic polarization. The leakage of soluble Pb and Ru species from the catalyst through the ionomer membrane will be evaluated. Other methods of applying polymer layers over the gas-fed electrodes or incorporating the polymer within the electrode will be discussed.

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References:

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